

Reactivity of 4-Phenyl-1,2,4-triazoline-3,5-dione and Diethylazocarboxylate in [4+2]-Cycloaddition and Ene Reactions: Solvent, Temperature, and High-Pressure Influence on the Reaction Rate

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Abstract

© 2015 Wiley Periodicals, Inc. We have studied the solvent, temperature, and pressure influences on the reaction rates of cyclic and acyclic N=N bonds in the Diels-Alder and ene reactions. The transfer from N-phenylmaleimide (9) to a structural analogue, 4-phenyl-1,2,4-triazoline-3,5-dione (2), is accompanied by the rate increase in five to six orders of magnitude in the Diels-Alder reactions with cyclopentadiene (4) and 9,10-dimethylantracene (5), whereas the transfer from dimethyl fumarate (10) to diethyl azodicarboxylate (1) increases only in one to two orders of magnitude. The ratio of the reaction rate constants $(2 + 4)/(1 + 4)$ is very large (5.2×10^7) and almost the same (5.3×10^7) as in the ene reactions with tetramethylethylene (7), $(2 + 7)/(1 + 7)$. It has been observed that the N=N bond in reagent 2 has strong electrophilic, and its N-N moiety in the transition state has nucleophilic properties, which results from the analysis of the solvation enthalpy transfer of reagents, activated complex, and adduct in the Diels-Alder reaction of 2 with anthracene 22.

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